PATENT SPECIFICATION (11) 1368495

(54) HAIR SETTING COMPOSITIONS

(71) We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation organized and existing under the Laws of the State of Delaware, United States of America, of 2501 Hudson Road, Saint Paul, Minnesota 55101, United States of America, do hereby declare that the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to temporary hair setting compositions.

Two principal processes have been employed in the art of hair setting. One involves permanent waving in which the configuration of hair fibres is substantially permanently changed by means of chemical agents which react with the fibres to achieve the desired permanently waved configuration. The other involves imparting a temporary set to hair fibres by application of lacquers or polymer compositions to hold the fibres in a predetermined position.

The principal properties desirable in temporary hair setting compositions are high curl retention, resistance to accumulation of static electricity, ability to be combed with ease, and high sheen. Temporary hair-setting compositions typically comprise solutions of polymers and copolymers of vinyl pyrrolidone, and polymeric quaternary ammonium and acid salts.

It is an object of the present invention to provide temporary hairsetting compositions which possess the desired properties.

Therefore according to the invention there is provided a temporary hair setting composition comprising an aqueous solution containing 0.25 to 10% by weight of a zwitterionic polymer, or its hydrochloride addition salt, obtained by polymerising a betaine monomer either alone or together with a copolymerisable monomer other than an ethylenically unsaturated amide or by copolymerizing an unsaturated amine with an unsaturated carboxylic acid, the polymer having a viscosity in the range 1,000 to 25,000 cP at 24% by weight solids in water at 24°C measured with a Brookfield Viscometer.

Also according to the invention there is provided a method of setting hair comprising the sequential steps of moistening the hair, applying a temporary hair setting composition comprising an aqueous solution containing 0.25 to 10% by weight of a zwitterionic polymer, or its hydrochloride addition salt, containing carboxylate and ammonium functionality and having a viscosity in the range 1,000 to 25,000 cP at 24% by weight solids in water at 24°C measured with a Brookfield Viscometer, arranging the hair into a desired configuration and drying the hair.

The temporary hair setting compositions of the present invention have excellent anti-static behaviour, good comb-out and sheen, and are easily removed from hair fibres by shampooing, but do not lose their excellent curl retention at high relative humidity conditions.

Zwitterionic monomers useful to provide homopolymers and copolymers suitable for hair setting have the general formula

$$R^1—(CH_2)_x—\overset{\oplus}{N}—(CH_2)_y—\overset{O}{\overset{\|}{C}}—O^{\ominus}$$
$$\underset{R^3}{\overset{R^2}{|}}$$
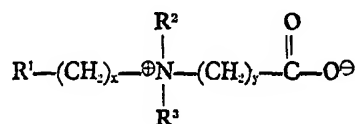
wherein R^1 represents an addition polymerizable unsaturated group, which permits homopolymerization of the monomer or copolymerization with other polymerizable monomers. Such polymerizable unsaturated groups are preferably selected from acryloxy, methacryloxy, acrylamido, and methacrylamido groups, x and y represent an integer from 1 to 3 inclusive to provide methylene, ethylene, or propylene groups in the polymer backbone, groups larger than 3

carbon atoms reducing the water solubility of the resultant polymer such that it is not useful as a hair setting composition. R^3 and R^3 represent methyl, ethyl, or propyl radicals, larger alkyl radicals also reducing the water solubility of the polymer. Typical zwitterionic monomers useful in preparing homopolymers or copolymers useful in the hair setting compositions of the invention are, for example, N - (beta - methacryloxyethyl) - beta - dimethylamino propionate betaine, and N - (beta - methacrylamidoethyl) - beta - dimethyl amino propionate betaine. Zwitterionic monomers of the aforementioned type may be prepared by methods known to the art.

As previously mentioned, zwitterionic monomers may either be homopolymerized or copolymerized with other polymerizable monomers to provide the zwitterionic polymers useful for setting hair, the effect of the zwitterionic group remaining effective even when relatively large proportions of comonomer are used. Generally, for most effective results, the non-zwitterionic monomer component should comprise less than about 90% by weight, preferably less than about 80% by weight of the desired copolymer to retain the properties necessary for setting hair. Typical water-soluble monomers suitable for copolymerization are such as, for example, vinyl pyrrolidone, dimethylaminoethyl acrylate, · dimethylaminoethyl methacrylate, beta diethylaminoethyl acrylate, and diethylaminoethyl methacrylate.

A preferred temporary hair setting composition of the invention comprises an aqueous solution containing between 1 and 5% by weight of a copolymer comprising a 80/20 mole ratio of units of beta - dimethyl aminoethyl methacrylate and N - (beta - methacryloxyethyl) - beta - dimethyl amino propionate betaine, 80% neutralised with hydrochloric acid.

Other monomers which are not water-soluble such as, for example, vinyl acetate, may also be copolymerized with the previously mentioned zwitterionic monomers to provide copolymers useful for setting hair. However, substantially less of this type of non-zwitterionic monomer is utilized so as to maintain the requisite solubility.

Other zwitterionic polymers containing carboxylate and ammonium functionality and useful in the invention are the internally neutralized acid salts obtained by copolymerizing an unsaturated amine with an unsaturated carboxylic acid.

Preferred internally neutralized acid salts are the copolymers of acrylic acid or methacrylic acid with dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, diethylaminoethyl methacrylate, or diethylaminoethyl acrylate. These internally neutralized acid salts may contain other copolymerizable monomer components and may contain ammonium or carboxylate functionality in excess of the stoichiometric amounts necessary for obtaining internal neutralization.

A solution of zwitterionic polymer, to be useful in setting hair, should be sufficiently viscous to remain on hair fibres when applied thereto, but be sufficiently thin to effectively wet the hair fibres. The previously disclosed zwitterionic polymers containing both carboxylate and ammonium functionalities and useful for setting hair have been found to have a viscosity in the range 1,000 to 25,000 cP, when tested at 24% by weight solids in water, with a Brookfield Viscometer. To provide hair setting compositions having desirable properties, the zwitterionic polymers have been found to be most effective when diluted to 0.25 to 10 percent by weight in water, preferably 1 to 5 percent. Alcohol may be used as a co-solvent with water, particularly when the zwitterionic polymer is a copolymer containing a non-water soluble monomer component. Polymers of viscosities higher than those mentioned or hair setting solutions having a higher zwitterionic polymer content provide a stiffer curl which is more difficult to comb-out and cause the hair fibres to feel slippery during application.

It has also been found that addition of a small amount of zwitterionic polymer to prior art aqueous hair setting compositions containing a water-soluble polymer improves their curl retention and antistatic behavior. Addition of as little as 0.25 percent by weight of zwitterionic polymer, to a hair-setting composition has been found effective. Additions of zwitterionic polymer which provide compositions having a solids content greater than about 10 percent by weight increase the comb-out to undesirably high levels.

The effectiveness of zwitterionic polymers for use in hair setting compositions is readily determined by means of a curl retention test which also provides information with respect to antistatic behavior, comb-out, and sheen. In conducting the test, a predetermined weight of human hair (approximately 6 inch length) is shampooed, rinsed with water, saturated with the respective hair setting composition being tested, followed by combing of the hair swatch four times. Each hair swatch is then wound on a hair roller, secured with bobby pins and thereafter dried at 140°F (60°C) for approximately two and one-half hours. Immediately following drying, the hair swatches are unwound from the rollers and combed five times with a brush, after which the curled test swatch is ready for determination of curl retention.

Ten hair swatches are prepared for each hair setting composition to be tested. The initial combed out hair length is recorded and the test swatches placed in a high relative

humidity test environment (about 85% relative humidity at about 75°F (24°C) for one hour was used here). The change in curl length is observed immediately after the period of time in humidity chamber, the precent of curl retention being calculated by the formula

$$\text{Curl Retention (\%)} = \frac{L - L_t}{L - L_o} \times 100$$

Where L is the length of the hair fully extended, L_t is the length of the hair when curled before exposure to the humidity environment, and L_o is the length of the hair after exposure to the high humidity environment. Because factors such as humidity in the drying oven, etc. cause results to be somewhat different for tests conducted on different days, all compositions are compared relative to a control sample evaluated at the same time. The percent curl retention for each hairsetting composition is then divided by the percent curl retention of the control and multiplied by 100 to obtain the relative curl retention. The composition of Example 1 was used as a control in each instance.

The followingExamples, in which all parts and percent solids are by weight unless otherwise indicated, illustrate the preparation of the hair setting compositions of the invention. Example 1 illustrates a control composition.

Example 1

As a control, poly - beta - dimethylaminoethyl methacrylate fully quaternized with methyl bromide was prepared and evaluated as a hair-setting lotion at 3% solids by weight in water. When tested by the previously described method, a relative curl retention of 100 was obtained.

Example 2

This Example illustrates the preparation of a hair setting composition utilizing a zwitterionic polymer comprising an 80:20 mole ratio copolymer of beta - dimethyl aminoethyl methacrylate and N - beta - methacryloxyethyl) - beta - dimethyl amino propionate betaine.

A polymerization flask fitted with a stirrer, nitrogen inlet, thermocouple, and addition funnel, was charged with 2842 grams of water, 315.2 grams of 37% hydrochloric acid in water, 618 grams of beta - dimethylaminoethyl methacrylate, and 225.2 grams of N - (beta - methacryloxyethyl) - beta - dimethylamino propionate betaine. The solution, with stirring, was evacuated to boiling for about 30 minutes, the flask purged with nitrogen, and the solution heated to 60°C for 16 hours, during which time 130 ml. of water containing 40 grams of $K_2S_2O_8$ was added in four equal portions about 30 minutes apart. The resultant polymer solution had a Brook-

field viscosity of 16,600 cP measured at 24% by weight solids in water at 24°C (#4 spindle at 30 RPM).

The polymer, at 3% solids in water, was evaluated as a hair setting resin by the previously described test method, a relative curl retention of 148, moderate comb-out, good sheen, and low static retention being obtained.

Example 3

This Example describes the preparation of a 50:50 mole ratio copolymer of acrylic acid and beta - dimethylaminoethyl methacrylate and the testing of a hair setting composition prepared therefrom. A polymerization flask equipped as in Example 2 was charged with 68.6 grams of beta - dimethylaminoethyl methacrylate, 31.4 grams of acrylic acid, 400 grams of distilled water, 0.4 grams of $K_2S_2O_8$, and the flask evacuated to boiling for a few minutes. The flask was pressurized with nitrogen and heated to 60°C. As the mixture thickened, it was diluted with water to 6.7% solids. This solution had a Brookfield viscosity of 600 cP (at 6.7% solids at 25°C), equivalent to 1400 cP measured at 24% by weight solids in water at 24°C (spindle 4 at 30 RPM).

The polymer at 4% solids in water, was evaluated as a hair setting resin by the previously described test method, a relative curl retention of 153, moderate comb-out, good sheen and low static retention being obtained.

Example 4

This Example describes the preparation of an 80:20 mole ratio copolymer of N - (beta - methacryloxyethyl) - beta - dimethylaminopropionate betaine and vinyl acetate and the testing of a hair setting composition prepared therefrom.

A polymerization flask equipped as in Example 2 was charged with 45.7 grams of N - (beta - methacryloxyethyl) - beta - dimethylaminopropionate betaine, 180 grams of distilled water, 4.3 grams of vinyl acetate in 20 grams of methanol, 0.4 grams of $K_2S_2O_8$, and the solution evacuated to boiling for a few minutes. The flask was pressurized with nitrogen and heated to 60°C for 4 hours. 100 Grams more water was added when the solution became too thick to stir efficiently. The viscosity of the polymer measured at 24% by weight solids in water at 24°C with a Brookfield viscometer is within the required range.

The polymer as a 2% solids water-alcohol solution containing 20% ethyl alcohol by weight was evaluated as a hair setting resin by the previously described test method, a relative curl retention of 155, moderate comb-out, good sheen, and low static retention being obtained.

Example 5

This Example describes the preparation of a 50:50 mole ratio copolymer of N - beta - methacryloxyethyl) - beta - dimethyl aminopropionate betaine and trimethyl beta - methacryloxyethyl ammonium methyl sulphate and testing of a hair setting composition prepared therefrom.

A polymerization flask equipped as in Example 2 was charged with 28.6 grams of N - (beta - methacryloxyethyl) - beta - dimethyl aminopropionate betaine, 88.9 grams of a 40% solids solution in water of trimethyl beta - methacryloxyethyl ammonium methyl sulphate, 202.5 grams of distilled water, and 0.235 grams $K_2S_2O_8$. The solution was evacuated to boiling, pressurized with nitrogen, and heated to 60°C for 2 hours. The viscosity of the polymer measured at 24% by weight solids in water at 24°C with a Brookfield viscometer is within the required range.

The polymer, at 4% solids in water provided an excellent hair setting lotion having curl retention, good sheen, moderate comb-out and low static retention.
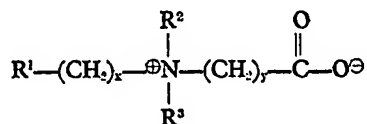
Example 6

An 80:20 mole ratio copolymer of N - (beta - methacryloxyethyl) - beta - dimethyl aminopropionate betain and trimethyl beta - methacryloxyethyl ammonium methyl sulphate was prepared by the technique described in Example 5 and tested as a hair setting composition at 4% solids in water. The viscosity of the polymer measured at 24% by weight solids in water at 24°C with a Brookfield viscometer is within the required range. The polymer was found to provide an excellent hair setting lotion having excellent curl retention, sheen, comb-out, and low static behavior.

WHAT WE CLAIM IS: —

1. A method of setting hair comprising the sequential steps of moistening the hair, applying a temporary hair setting composition comprising an aqueous solution containing 0.25 to 10% by weight of a zwitterionic polymer, or its hydrochloride addition salt, containing carboxylate and ammonium functionality and having a viscosity in the range 1000 to 25000 cP at 24% by weight solids in water at 24°C measured with a Brookfield Viscometer, arranging the hair into a desired configuration and drying the hair.

2. A method as claimed in Claim 1 in which the zwitterionic polymer is derived from a monomer having the general formula

$$R^1\text{---}(CH_2)_x\text{---}\overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle R^3}{|}}{\oplus N}}\text{---}(CH_2)_y\text{---}\overset{\overset{\displaystyle O}{\|}}{C}\text{---}O^\ominus$$

in which R^1 represents an additional polymerisable unsaturated group, x and y are integers from 1 to 3 inclusive and R^2 and R^3 represent methyl, ethyl or propyl radicals.

3. A method as claimed in Claim 1 in which the zwitterionic polymer is obtained by copolymerizing an unsaturated amine with an unsaturated carboxylic acid.

4. A method as claimed in Claim 1 or Claim 2 in which the zwitterionic polymer is a polymer of N - (beta - methyacryloxy - ethyl) - beta - dimethyl aminopropionate betaine.

5. A method as claimed in Claim 1 in which the zwitterionic polymer is a copolymer comprising an 80:20 mol ratio of units of beta - dimethylaminoethyl methacrylate and N - (beta - methacryloxyethyl) - beta - dimethyl aminopropionate betaine.

6. A method of setting hair as claimed in Claim 1 substantially as herein described with reference to any of Examples 2 to 6.

7. A temporary hair setting composition comprising an aqueous solution containing 0.25 to 10% by weight of a zwitterionic polymer, or its hydrochloride addition salt, obtained by polymerizing a betaine monomer either alone or together with a copolymerisable monomer other than an ethylenically unsaturated amide or by copolymerizing an unsaturated amine with an unsaturated carboxylic acid, the polymer having a viscosity in the range 1000 to 25000 cP at 24% by weight solids in water at 24°C measured with a Brookfield Viscometer.

8. A temporary hair setting composition as claimed in Claim 7 in which the zwitterionic polymer is a polymer of N - (beta - methacryloxyethyl) - beta - dimethylaminopropionate betaine.

9. A temporary hair setting composition as claimed in Claim 8 in which the betaine polymer is a homopolymer.

10. A temporary hair setting composition as claimed in Claim 7 in which the zwitterionic polymer is a copolymer of N - (beta - methacryloxyethyl) - beta - dimethylpropionate betaine with beta - dimethyl aminoethyl methacrylate.

11. A temporary hair setting composition as claimed in Claim 10 comprising an aqueous solution containing between 1 and 5% by weight of a copolymer comprising a 80/20 mol ratio of units of beta - dimethyl amino-ethyl methacrylate and N - (beta - methacryloxyethyl) - beta - dimethyl amino-propionate betaine, 80% neutralised with hydrochloric acid.

12. A temporary hair setting composition comprising an aqueous solution of a water-soluble polymer and at least 0.25% by weight of a zwitterionic polymer, or its hydrochloride addition salt, containing carboxylate and ammonium functionality and having a vis-

cosity in the range 1000 to 25000 cP at 24% by weight solids in water at 24°C measured with a Brookfield Viscometer, the composition containing no greater than 10% by weight solids.

13. A temporary hair setting composition as claimed in any of Claims 7 to 12 in which the zwitterionic polymer contains ammonium or carboxylate functionality in excess of the stoichiometric amounts necessary for obtaining internal neutralisation.

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